

RECEIVED
SEP 11 2003
TC 1700


In the matter
of European Patent Application
No. 96306260.9
of Nippon Shokubai Co., Ltd.

D E C L A R A T I O N

I, Nobuko Saito of HATTA & ASSOCIATES, Dia Palace
Nibancho, 11-9, Nibancho, Chiyoda-ku, Tokyo, Japan do
solemnly and sincerely declare:

1. That I am well acquainted with the English and Japanese languages, and
2. That the attached document is a full and faithful translation into the English language made by me of the accompanying certificate of Japanese Patent Application No. 7-220072 duly certified by Commissioner of Patent Office to the best of my knowledge and belief.

Declared at Tokyo, Japan on this 20th day of May, 1997.



Nobuko Saito

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the
following application as filed with this Office.

Date of Application : August 29, 1995

Application Number : 07-220,072

Applicant(s) : Nippon Shokubai Co., Ltd.

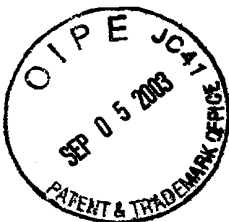
August 16, 1996

Commissioner,

Patent Office

Hisamitsu ARAI (Seal)

Certificate HEI 08-3055332



RECEIVED
SEP 11 2003
TC 1700

[Document's Name] APPLICATION FOR PATENT

[Docket Number] 00005008

[Filing Date] August 29, 1995

[Address To:] The Commissioner of the Patent Office

5 [International Patent Classification] C07D207/448

[Title of the Invention] ACRYLONITRILE SOLUTIONS OF MALEIMIDES AND METHOD FOR PREPARATION THEREOF

[Number of Claims] 5

10 [Inventor]

[Domicile or Residence] c/o Nippon Shokubai Co., Ltd.,
992-1, Aza-Nishioki, Okihama,
Aboshi-ku, Himeji-shi, Hyogo-ken

[Name] Kazuo KISHINO

15 [Inventor]

[Domicile or Residence] c/o Nippon Shokubai Co., Ltd.,
992-1, Aza-Nishioki, Okihama,
Aboshi-ku, Himeji-shi, Hyogo-ken

[Name] Yuichi KITA

20 [Inventor]

[Domicile or Residence] c/o Nippon Shokubai Co., Ltd.,
992-1, Aza-Nishioki, Okihama,
Aboshi-ku, Himeji-shi, Hyogo-ken

[Name] Kinichi NAKAYAMA

25 [Applicant]

[Identification Number] 000004628

[Zip Code] 541

[Domicile or Residence] 1-1, Koraihashi 4-chome, Chuo-ku,
Osaka-shi, Osaka-fu

30 [Name] Nippon Shokubai Co., Ltd.

[Representative] Shoso TANAKA

[Identification of Official Fee]

[Number of Ledger of Deposit Account] 008291

35 [Sum to be Paid] 21,000 YEN

[List of Things to be Submitted]

[Name of Thing]	Specification	1
[Name of Thing]	Abstract	1
[Demand of Proof]	Yes	

[DOCUMENT'S NAME] SPECIFICATION

[TITLE] ACRYLONITRILE SOLUTIONS OF MALEIMIDES
AND METHOD FOR PREPARATION THEREOF

[CLAIMS]

5 [Claim 1] An acrylonitrile solution of maleimides, characterized by the fact that, in a forced coloration test, the values, ΔL , Δa , and Δb , to be calculated in accordance with the following formulas:

$\Delta L = |L \text{ value after test} - L \text{ value before test}|$ (Absolute value)

10 $\Delta a = |a \text{ value after test} - a \text{ value before test}|$ (Absolute value)

$\Delta b = |b \text{ value after test} - b \text{ value before test}|$ (Absolute value)

are respectively not more than 5, not more than 5, and not more than 10.

[Claim 2] A method for the preparation of an acrylonitrile
15 solution set forth in claim 1, characterized in that said acrylonitrile solution of maleimides has a water content of not more than 0.1% by weight.

[Claim 3] A method for the preparation of an acrylonitrile
20 solution set forth in claim 1, characterized in that said acrylonitrile solution of maleimides allows the presence therein of at least one member selected among hindered phenols and at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides.

[Claim 4] A method for the preparation of an acrylonitrile
25 solution set forth in claim 1, characterized in that said acrylonitrile solution of maleimides has a water content of not more than 0.3% by weight and allows the presence therein of at least one member selected among hindered phenols, or at least one member selected from the group consisting of phosphorous esters,
30 phosphoric esters, and phosphoric acid amides.

[Claim 5] An acrylonitrile-maleimides-containing copolymer obtained by the use of the acrylonitrile solution of maleimides set

forth in claim 1.

[Detailed Description of the Invention]

[0001]

[Technical Filed the Invention Belongs to]

5 The present invention relates to acrylonitrile solutions of maleimides, a method for the preparation thereof, and acrylonitrile-maleimides containing copolymers obtained by the use of the acrylonitrile solutions.

[0002]

10 [Prior Art]

 The maleimides represented by N-phenyl maleimide and the like are used widely as a heat resistance enhancer for such acrylonitrile based copolymers as acrylonitrile-butadiene-styrene (ABS) resin, acrylonitrile-acrylic rubber-styrene (AAS) resin,
15 acrylonitrile-styrene (AS) resin, and acrylonitrile-chlorinated polyethylene-styrene (ACS) resin in the copolymerization with the monomer which constitutes the above-mentioned resins. In this invention, the term "acrylonitrile-maleimides containing copolymer" refers to acrylonitrile type copolymers containing
20 maleimides.

[0003]

 The maleimides which are in a solid state at room temperature have been heretofore handled generally in such forms as powder, flakes, and tablets. The maleimides in these solid forms, however,
25 undergo gradual comminution and yield minute particles copiously during the course of transportation and consequently give rise to numerous problems such as deterioration of the work environment. For the solution of these problems, the present inventors have proposed a method for enabling the maleimides to be handled securely
30 in the form of acrylonitrile solutions obtained in advance by dissolving the maleimides together with a polymerization inhibitor in acrylonitrile (JP-B-03-12,057). Since this method which

permits the maleimides to be handled in the form of acrylonitrile solutions is excellent in having solved the problems mentioned above, it has been finding growing acceptance for industrial applications.

[0004]

5 Further, the present inventors have also proposed as a method for handling maleimides in an acrylonitrile solution a method which comprises adjusting an acid content of maleimides in an acrylonitrile solution to 0.3% by weight (JP-A-64-61,456) and a
10 method which comprises adjusting an acid content of maleimides in an acrylonitrile solution to not more than 0.3% by weight and coexisting a polymerization inhibitor therein (JP-A-1-250,348), etc. These methods allow an acrylonitrile solution of maleimides to be handled safely and stably while preventing a metal material from being eroded with the acrylonitrile solution.

15 [0005]

An acrylonitrile solution of maleimides can be used in combination with another monomer in the production of the above-mentioned acrylonitrile based copolymers (the acrylonitrile as the solvent for the acrylonitrile solutions of maleimides
20 constitutes itself the source of the acrylonitrile component of the acrylonitrile based copolymers). When the acrylonitrile solution of maleimides as the raw material is colored or opacified, the obtained acrylonitrile-maleimides-containing copolymer has bad color tone and has markedly impaired marketability. For the
25 purpose of improving the finished products in marketability, the standards or demands imposed on the color or opacification of the acrylonitrile solutions of maleimides have been decisively gaining in exactitude in recent years. An acrylonitrile solution of maleimides which is transparent, is not colored nor opacified during
30 the course of handling, and has excellent stability is strongly demanded.

[0006]

Although the methods for handling an acrylonitrile solution of maleimides as described above have solved the above-mentioned problems to some extent, the recent, exact demands as mentioned above are not always met satisfactorily.

5 [0007]

[Problems the Invention is to Solve]

An object of this invention, therefore, is to provide an acrylonitrile solution of maleimides which is transparent, is not colored nor opacified during the course of handling, and has
10 excellent stability.

[0008]

Another object of this invention is to provide a method for preparing of the acrylonitrile solution of maleimides as mentioned above.

15 [0009]

Yet another object of this invention is to provide a acrylonitrile-maleimides-containing copolymer with excellent color tone which is obtained by using the acrylonitrile solution of maleimides as mentioned above.

20 [0010]

In the content of this specification, the term "handling" refers to the transportation as by tank lorries, the storage as in tanks, and the conveyance as by the pipeline including pipe, valves, and nozzles (such as, for example, the polymer-feeding line from
25 the storage tank for the acrylonitrile solutions of maleimides).

[0011]

[Means to Solve the Problems]

The present invention relates to an acrylonitrile solution of maleimides, characterized by the fact that, in a forced
30 coloration test, the values, ΔL , Δa , and Δb , to be calculated in accordance with the following formulas are respectively not more than 5, not more than 5, and not more than 10.

[0012]

In this case,

$\Delta L = |L \text{ value after test} - L \text{ value before test}|$ (Absolute value)

$\Delta a = |a \text{ value after test} - a \text{ value before test}|$ (Absolute value)

5 $\Delta b = |b \text{ value after test} - b \text{ value before test}|$ (Absolute value)

The present invention concerns a method for the preparation of the above acrylonitrile solution wherein the acrylonitrile solution of maleimides has a water content of not more than 0.1% by weight.

10 [0013]

The present invention also concerns a method for the preparation of the above acrylonitrile solution wherein the acrylonitrile solution of maleimides allows the presence therein of at least one member selected among hindered phenols and at least
15 one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides.

[0014]

The present invention further concerns a method for the preparation of the above acrylonitrile solution wherein the
20 acrylonitrile solution of maleimides has a water content of not more than 0.3% by weight and allows the presence therein of at least one member selected among hindered phenols, or at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides.

25 [0015]

The present invention further concerns an acrylonitrile-maleimides-containing copolymer obtained by the use of the acrylonitrile solution as mentioned above.

[0016]

30 [Embodiments]

The acrylonitrile solution of maleimides according to this invention has the values, ΔL , Δa , and Δb , which are respectively

5 deferences between the values, L, a, and b before and after
undergoing the forced coloration test under forced coloring
conditions in a forced coloration test of not more than 5, not more
than 5, and not more than 10, respectively. The acrylonitrile
solution of maleimides having such values, ΔL , Δa , and Δb , has
rarely colored and opacified, and has excellent stability. The
values, ΔL , Δa , and Δb , are particularly preferably not more than
1, not more than 1, and not more than 2, respectively.

[0017]

10 The method for determining the L, a, and b values and the method
for the forced coloration test are as followed.

[0018]

L, a, and b values

By the use of a colorimeter produced by Nippon Denshoku Kogyo
15 K.K. and marketed under product code of "Σ-80 type", a sample of
the acrylonitrile solution of maleimide is adjusted to a
concentration of 30% by weight and subsequently measured for the
L, a, and b values by the transmission mode. A commercially
available acrylonitrile (guaranteed reagent) is used as a control
20 and the cell used for the test has a thickness of 10 mm.

[0019]

FORCED COLORATION TEST

A sample of the acrylonitrile solution of maleimide is
introduced in a Pyrex test tube, with a size of 18 mm in inside
25 diameter and 180 mm height. Then, into the solution, a
preparatorily polished test piece made of SUS 304 and measuring 50
mm in length, 10 mm in width, and 2 mm in thickness is placed. The
test tube is immersed in an oil bath set at 70°C and allowed to stand
therein for three days (72 hours), and extracted from the test tube.
30 The acrylonitrile solution is subjected to the determination of the
values, L, a, and b.

[0020]

Typical examples of the maleimides which are used in this invention include maleimide, N-methyl maleimide, N-ethyl maleimide, N-hexyl maleimide, N-octyl maleimide, N-dodecyl maleimide, N-benzyl maleimide, N-cyclohexyl maleimide, N-phenyl maleimide, 5 N-nitrophenyl maleimide, N-methoxyphenyl maleimide, N-methylphenyl maleimide, N-carboxyphenyl maleimide, N-hydroxyphenyl maleimide, N-chlorophenyl maleimide, N-dimethylphenyl maleimide, N-dichlorophenyl maleimide, N-bromophenyl maleimide, N-dibromophenyl maleimide, N-10 trichlorophenyl maleimide, and N-tribromophenyl maleimide, for example. Among other maleimides cited above, N-phenyl maleimide proves particularly advantageous for the use contemplated herein. This invention does not discriminate the maleimide to be used therein on account of the method to be adopted for the production 15 thereof. The maleimides obtained by varying methods can be used herein. The maleimides produced by some, if not all, of these methods contain a residual acid component, for example an acid catalyst to be used in the reaction. This invention tolerates the presence in the maleimide of up to about 5% by weight of such an 20 acid component. It nevertheless prefers the maleimide to be used after being refined, for example, by washing with water and distillation, until the content of the acid component thereof falls not more than 0.3% by weight.

[0021]

25 The dissolution of maleimide in acrylonitrile can be implemented by any arbitrary method such as, for example, throwing the maleimide into acrylonitrile. Typically, a method which comprises filling maleimide in a container substantially sealed hermetically and equipped with nozzles for liquid-circulation at 30 upper and lower parts thereof, and circulating an acrylonitrile solution with heated from the upper nozzle to the lower nozzle thereby dissolving maleimide therein (JP-B-06-70,009), and a method

which comprises filling maleimide in a container substantially sealed hermetically and equipped with one nozzle for liquid-circulation, and repeatedly introducing a heated acrylonitrile solution through the nozzle thereby dissolving maleimide therein (JP-B-06-70,008) may be cited. Properly, the solution of maleimide is carried out at a temperature not exceeding the boiling point of acrylonitrile (78.5°C). Since acrylonitrile has a high vapor pressure, it is generally advantageous to carry out the dissolution process at a temperature in the range of 30 to 70°C. Generally, the temperature at which the acrylonitrile solution is handled is generally not more than 70°C.

[0022]

The materials of which the facilities (including pipelines) for handling the acrylonitrile solution are made are not limited particularly. The surfaces of the facilities exposed to the acrylonitrile solution may be passivated by glass lining, ceramic coating, etc. For handling the acrylonitrile solution on a commercial scale, it is economically favorable to use facilities which are made of such a general-purpose industrial material as carbon steel or stainless steel.

[0023]

The concentration of maleimide in the acrylonitrile solution is not particularly limited. It can be suitably selected in consideration of such factors as the temperature of handling, the form of handling (such as transportation or storage), the kind of the acrylonitrile based copolymer to be produced with the acrylonitrile solution, the method of this production, and the production conditions. In some cases, the concentration of maleimide is preferably high as when the acrylonitrile solution is used for the production of an acrylonitrile based copolymer having a high maleimide content, for example. Generally, the concentration of maleimide is in the range of 40 to 90% by weight.

[0024]

The acrylonitrile solution of maleimide of this invention is transparent. The acrylonitrile solution of maleimide of this invention has particularly appropriately the values of L, a, and b (i.e. the values of L, a, and b to be determined before the forced color test) in the following ranges: L = 90 to 100, a = -10 to -30, and b = 30 to 50.

[0025]

Water is contained in industry grade acrylonitrile which is usually used as a solvent in an amount in the approximate range of 0.5 to 1% by weight. In accordance with the long study by the present inventors, the coloration or opacification of the acrylonitrile solution of maleimide is caused by the presence of water in the acrylonitrile solution, namely the presence of water contained in the acrylonitrile solution used as the solvent. On other words, one example will be described by using N-phenyl maleimide as the maleimide as below. N-phenyl maleimide is hydrolyzed to form N-phenyl maleinamic acid which is not dissolved in acrylonitrile. The N-phenyl maleinamic acid is subjected to the further hydrolysis into maleic acid and aniline, among which maleic acid has strong corrosion properties. The maleic acid erodes an equipment handling an acrylonitrile solution, particularly a surface of an equipment made of carbon steel or stainless steel, consequently causing the formation of metal ions and radical active species (hydroperoxide). This hydroperoxide induces the formation of various aniline derivatives or polymers with low polymerization degree. Further, the aniline and the aniline derivatives or polymers with low polymerization degree is considered to induce the coloration or opacification of the acrylonitrile solution. It, however, should be noted that the present invention is not limited by the above theoretical hypothesis.

[0026]

The acrylonitrile solution of maleimide which has the deferences, ΔL , Δa , and Δb , before and after the forced color test (hereinafter referred to simply as "before and after test" in some cases) of not more than 5, not more than 5, and not more than 5, respectively, preferably, more than 1, not more than 1, and not more than 2, respectively, can be efficiently produced by the methods which will be described specifically hereinbelow. These methods are adopted advantageously when the acrylonitrile solution of maleimide is handled with facilities which are made of such a general-purpose industrial material as carbon steel or stainless steel.

[0027]

<Method A>

Method A comprises adjusting the water content in the acrylonitrile solution of maleimide to not more than 0.1% by weight (refer to Example 9). The acrylonitrile solution of this invention cannot be prepared when the water content exceeds 0.1% by weight (refer to Controls 1 to 3). For the purpose of lowering the water content in the acrylonitrile solution to a level of not more than 0.1% by weight, since the maleimide contains substantially no water, it suffices to lower the water content in the acrylonitrile used as the solvent to a level not more than 0.1% by weight. The water content in the acrylonitrile can be adjusted by any of the known methods such as, for example, precision distillation, physical adsorption by the use of silica gel or molecular sieve, or dehydration by the use of anhydrous sodium sulfate or anhydrous magnesium sulfate. Appropriately, the water content in the acrylonitrile solution is as low as possible. The lower limit of the water content is suitably decided in consideration of the transparency and stability of the acrylonitrile solution, and the economical cost.

It is particularly advantageous to lower the water content

in the acrylonitrile solution to a level of not more than 0.05% by weight. When the water content is thus lowered, the acrylonitrile solution to be prepared is such that the values of ΔL , Δa , and Δb thereof are respectively not more than 1, not more than 1, and
5 not more than 2.

[0028]

<Method B>

Method B resides in enabling the acrylonitrile solution to coexist with an antioxidant effective in precluding the generation
10 of hydroperoxide. As the antioxidant, at least one member selected among hindered phenols or at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides can be used by itself. It is, however, effective to use at least one member selected among hindered phenols in
15 combination with at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides. Thus, the Method B may be carried out according to two embodiments as follows.

[0029]

20 <Method B-1>

At least one member selected among hindered phenols and at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides are caused to exist in the acrylonitrile solution (refer to Example 11). In
25 this case, although the water content in the acrylonitrile solution is not particularly limited, in view point of the water content in the industry grade acrylonitrile, the upper limit thereof is approximately in the range of 0.5 to 0.6% by weight. The water content in the acrylonitrile solution is preferably low, and more
30 preferably adjusted up to 0.3% by weight.

[0030]

<Method B-2>

The water content in the acrylonitrile solution is lowered to a level of not more than 0.3% by weight and at least one member selected among hindered phenols, or at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides is caused to exist in the acrylonitrile solution (refer to Example 12).

[0031]

In the methods B-1 and B-2 mentioned above, the acrylonitrile solution which is more transparent and has superior stability can be prepared by lowering the water content in the acrylonitrile solution to a level of not more than 0.2% by weight, preferably to a level of not more than 0.1% by weight. Particularly when the water content in the acrylonitrile solution is lowered to a level of not more than 0.05% by weight, the acrylonitrile solution whose values of ΔL , Δa , and Δb are respectively not more than 1, not more than 1, and not more than 2 can be prepared.

[0032]

As typical examples of the hindered phenol mentioned above, 2,4-dimethyl-6-tert-butyl phenol, 4-tert-butyl catechol, 2,5-di-tert-butyl hydroquinone, 2-tert-dibutyl hydroquinone, 4,4'-thio-bis(6-tert-butyl-m-cresol), 2,4-bis(n-octylthio)-6-(4-hydroxy-3,5-di-tert-butyl anilino)-1,3,5-triazine, 2,2'-thiobis-(4-methyl-6-tert-butyl phenol), triethylene glycol-bis-[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl) propionate], pentaerythritol-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, 2,2-thio-diethylenebis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], 1,6-hexane diol-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene, N',N'-hexamethylenebis(3,5-di-tert-butyl-4-hydroxyhydrocinnamide),

and 3,5-di-tert-butyl-4-hydroxy-benzylphosphonate-diethyl ester may be cited.

[0033]

Among other hindered phenols enumerated above, 2,4-
5 dimethyl-6-tert-butyl phenol, 4-tert-butyl catechol, 2,5-di-
tert-butyl hydroquinone, 2-tert-dibutyl hydroquinone, 4,4'-
thio-bis(6-tert-butyl-m-cresol), 2,4-bis(n-octylthio)-6-(4-
hydroxy-3,5-di-tert-butyl anilino)-1,3,5-triazine, 2,2'-
thiobis-(4-methyl-6-tert-butyl phenol), and triethylene glycol-
10 bis-[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl) propionate] are
advantageously used.

[0034]

As typical examples of the phosphorous ester, triphenyl
phosphite, tris(nonylphenyl)phosphite, triethyl phosphite,
15 tris(2-ethylhexyl)phosphite, tridecyl phosphite, tris(tridecyl)
phosphite, tristearyl phosphite, diphenyl mono(2-ethylhexyl)
phosphite, diphenyl monodecyl phosphite, diphenyl monotridecyl
phosphite, dilauryl hydrogen phosphite, dilauryl hydrogen
phosphite, diphenyl hydrogen phosphite, tetraphenyl dipropylene
20 glycol phosphite, tetraphenyl tetra(tridecyl)pentaerythritol
tetraphosphite, tetra(tridecyl)-4,4'-isopropylidene diphenyl
phosphite, trilauryl trithiophosphite,
bis(tridecyl)pentaerythritol diphosphite, bis(nonylphenyl)
pentaerythritol phosphite, stearyl pentaerythritol diphosphite,
25 tris(2,4-di-tert-butylphenyl) phosphite, hydrogenated bisphenol
A-pentaerythritol phosphite polymer, and hydrogenated bisphenol
A-phosphite polymer may be cited.

[0035]

As typical examples of the phosphoric ester and phosphoric
30 acid amide, ethyldiethyl phosphonoacetate, ethyl acid phosphate,
beta-chloroethyl acid phosphate, butyl acid phosphate, butyl
pyrophosphate, butoxyethyl acid phosphate, 2-ethylhexyl acid

phosphate, di(2-ethylhexyl) phosphate, ethylene glycol acid phosphate, (2-hydroxyethyl)methacrylate acid phosphate, tris (2-chloroethyl) phosphate, tris(dichloropropyl)phosphate, octyl dichloropropyl phosphate, phenyldichloropropyl phosphate, 5 trimethyl phosphate, triethyl phosphate, tributyl phosphate, trioctyl phosphate, tricresyl phosphate, triphenyl phosphate, and hexamethyl phosphoric triamide may be cited.

[0036]

Among other phosphorous esters, phosphoric esters, and 10 phosphoric acid amides enumerated above, tris(nonylphenyl) phosphate, distearyl pentaerythritol diphosphite, tristearyl phosphite, and di(2-ethylhexyl) phosphate are advantageously used.

[0037]

The amount of at least one member selected among hindered 15 phenols mentioned above to be used is in the range of 0.0001 to 1% by weight, preferably 0.001 to 0.1% by weight, based on the amount of the maleimide. The amount of at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides mentioned above to be used is in the range 20 of 0.0001 to 1% by weight, preferably 0.001 to 0.1% by weight, based on the amount of the maleimide. When hindered phenol is to be used in combination with the phosphorous compound, the ratio of combination of the two members is not particularly limited. It may be properly decided so that the amounts of the two members involved 25 fall in the relevant ranges of use mentioned above.

[0038]

Among the combinations between the hindered phenols and the phosphorus compound, the following combinations are particularly advantageous: a combination of 4-tert-butyl catechol with distearyl 30 pentaerythritol diphosphite, and a combination of triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate] with distearyl pentaerythritol diphosphite.

[0039]

In Method A and Method B mentioned above, the acrylonitrile solution of maleimide which is more transparent and has superior stability can be prepared by defining the molecular oxygen concentration in the gaseous phase part of the acrylonitrile solution of maleimide within a specific range, or by adding a metal inactivating agent for the purpose of preventing the generation of the hydroperoxide as mentioned above. The typical examples of this method will be described below.

10 [0040]

<Method C>

The Method C comprises the Method A and Method B mentioned above which further comprises adjusting the molecular oxygen concentration in the gaseous phase part of the acrylonitrile solution (providing that the molecular oxygen concentration is obtained of the gas mixture excluding maleimide and acrylonitrile on the basis of volume; this remark similarly applies hereinafter) to a level in the range of 0.1 to 10% by volume. A deviation from the range mentioned above is unfavorable because the coloration or opacification will not be effectively precluded if the molecular oxygen concentration exceeds 10% by volume and the acrylonitrile solution of maleimide will suffer inclusion of monomers other than maleimide and acrylonitrile and incur opacification owing to the contamination of containers such as storage tanks if the molecular oxygen concentration is less than 0.01% by volume. It is, therefore, appropriate that the molecular oxygen concentration is in the range of 0.01 to 10% by volume, preferably 0.1 to 8% by volume, and more preferably 1 to 7% by volume. The gas mixture excluding maleimide and acrylonitrile mentioned above generally comprises molecular oxygen and such inert gases as nitrogen, carbon dioxide, helium, and argon. Since nitrogen is advantageously used as the inert gas, the gas mixture consisting of molecular oxygen and nitrogen may be

cited as an appropriate example of the gas mixture excluding maleimide and acrylonitrile. Now, the preferred embodiments will be cited below.

[0041]

5 <Method C-1>

The water content in the acrylonitrile solution is lowered to a level of not more than 0.1% by weight and, at the same time, the molecular oxygen concentration in the gaseous phase part of the acrylonitrile solution is adjusted to a level in the range of 0.01
10 to 10% by volume (refer to Example 13).

[0042]

<Method C-2>

At least one member selected among hindered phenols and at least one member selected from the group consisting of phosphorous
15 esters, phosphoric esters, and phosphoric acid amides are allowed to exist in the acrylonitrile solution of maleimide, and the molecular oxygen concentration in the gaseous phase part of the acrylonitrile solution is adjusted to a level in the range of 0.01 to 10% by volume (refer to Examples 1, 2, 3, and 6).

20 [0043]

<Method C-3>

The water content in the acrylonitrile solution is lowered to a level of not more than 0.3% by weight, at least one member selected among hindered phenols, or at least one member selected
25 from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides is allowed to exist in the acrylonitrile solution of maleimide, and the molecular oxygen concentration in the gaseous phase part of the acrylonitrile solution is adjusted to a level in the range of 0.01 to 10% by volume (refer to Example
30 10).

[0044]

In the Methods C-1 to C-3 mentioned above, the acrylonitrile

solution of maleimide which is more transparent and has superior stability can be prepared by lowering the water content in the acrylonitrile solution to a level of not more than 0.2% by weight, preferably 0.1% by weight. Particularly, the acrylonitrile solution whose values of ΔL , Δa , and Δb before and after test are respectively not more than 1, not more than 1, and not more than 2 can be prepared by lowering the water content in the acrylonitrile solution to a level of not more than 0.05% by weight.

[0045]

10 <Method D>

The Method D comprises the Method A to Method C mentioned above which further comprises allowing a metal-inactivating agent to exist in the acrylonitrile solution. As typical examples of the metal-inactivating agent mentioned above, N,N'-bis[3-(3,5-di-
15 tert-butyl-4-hydroxyphenyl) propionyl]hydrazine, 2,2'-oxamide bis[ethyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], N,N'-disalicylidene-1,2-propane diamine, benzotriazole, tollyl triazole, tollyl triazole-potassium salt, and mercapto benzotriazole-sodium salt may be cited. Among other metal-
20 inactivating agents enumerated above, N,N'-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionyl] hydrazine, and 2,2'-oxamide bis[ethyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] are advantageously used. These metal-inactivating agents may be used either singly or in the form of a mixture of two or more members.
25 The amount of the metal-inactivating agent to be added is in the range of 0.0001 to 1% by weight, preferably 0.001 to 0.1% by weight, based on the amount of the maleimide. As concrete means to implement the addition of the metal-inactivating agent, the following embodiments may be cited.

30 [0046]

<Method D-1>

The water content in the acrylonitrile solution is lowered

to a level of not more than 0.1% by weight and the metal-inactivating agent is added (refer to Example 14).

[0047]

<Method D-2>

5 The water content in the acrylonitrile solution is lowered to a level of not more than 0.1% by weight, the molecular oxygen concentration in the gaseous phase part of the acrylonitrile solution is adjusted to a level in the range of 0.1 to 10% by volume, and the metal-inactivating agent is added (refer to Example 15).

10 [0048]

<Method D-3>

At least one member selected among hindered phenols and at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides are caused
15 to exist in the acrylonitrile solution and the metal-inactivating agent is added (refer to Example 4).

[0049]

<Method D-4>

20 The water content in the acrylonitrile solution is lowered to a level of not more than 0.3% by weight, at least one member selected among hindered phenols, or at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides is caused to exist in the acrylonitrile solution, and the metal-inactivating agent is added (refer to
25 Example 14).

[0050]

<Method D-5>

At least one member selected among hindered phenols and at least one member selected from the group consisting of phosphorous
30 esters, phosphoric esters, and phosphoric acid amides are caused to exist in the acrylonitrile solution, the molecular oxygen concentration in the gaseous phase part of the acrylonitrile

solution is adjusted to a level in the range of 0.1 to 10% by volume, and the metal-inactivating agent is added (refer to Examples 5, 7, and 8).

[0051]

5 <Method D-6>

The water content in the acrylonitrile solution is lowered to a level of not more than 0.3% by weight, at least one member selected among hindered phenols, or at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides is caused to exist in the acrylonitrile solution, the molecular oxygen concentration in the gaseous phase part of the acrylonitrile solution is adjusted to a level in the range of 0.1 to 10% by volume, and the metal-inactivating agent is added (refer to Example 17).

15 [0052]

In the Methods D-1 to D-6 mentioned above, the acrylonitrile solution of maleimide which is more transparent and has superior stability can be prepared by lowering the water content in the acrylonitrile solution to a level of not more than 0.2% by weight, preferably 0.1% by weight. Particularly, the acrylonitrile solution whose values of ΔL , Δa , and Δb before and after test are respectively not more than 1, not more than 1, and not more than 2 can be prepared by lowering the water content in the acrylonitrile solution to a level of not more than 0.05% by weight.

25 [0053]

The acrylonitrile solution of maleimide this invention whose values of ΔL , Δa , and Δb before and after test are respectively not more than 5, not more than 5, and not more than 10, preferably not more than 1, not more than 1, and not more than 2 is transparent, is not colored or opacified, and has excellent stability. By using this acrylonitrile solution of maleimide, therefore, an acrylonitrile-maleimide-containing copolymer with excellent color

tone can be obtained. To be specific, such acrylonitrile-maleimide-containing copolymers having excellent transparency and heat-resistance, as acrylonitrile-butadiene-styrene (ABS) resin, acrylonitrile-acrylic rubber-styrene (AAS) resin, acrylonitrile-styrene (AS) resin, and acrylonitrile-chlorinated polyethylene-styrene (ACS) resin each of which contains maleimide, can be obtained.

[0054]

These acrylonitrile-maleimide-containing copolymers can be easily produced by the known method except that the acrylonitrile solution of maleimide of this invention is used in place of the known acrylonitrile solution of maleimide. These acrylonitrile based copolymers, when necessary, can incorporate therein various known additives.

[0055]

[Examples]

Now, this invention will be described more specifically below with reference to working examples and controls. In the examples, the compound to be prepared by the following Synthesis Example was used as the N-phenyl maleimide.

[0056]

Synthesis Example

An N-phenyl maleamic acid obtained from aniline and maleic anhydride was left reacting in an o-xylene solvent at a temperature of not less than 130°C in the presence of an acid catalyst. The reaction was allowed to proceed while the water formed thereby was expelled in the form of a mixture with o-xylene from the system by distillation. The reaction mixture obtained by the resultant ring-closure conversion into imide was separated into an organic solvent layer containing therein N-phenyl maleimide and a catalyst layer. The organic solvent layer was washed with water. The organic solvent layer thus obtained was distilled under a reduced

pressure to expel o-xylene. The residue by the distillation was further distilled to obtain a yellow N-phenyl maleimide. This product, on analysis by liquid chromatography, was found to have a purity of not less than 99.5%.

5 [0057]

Example 1

Two Pyrex test tubes with a size of 18 mm in inside diameter and 180 in height, were prepared. In each of the test tubes, an acrylonitrile solution having an N-phenyl maleimide concentration
10 of 60% by weight, a water content of 0.1% by weight, an antioxidant (a-1) content of 500 ppm (based on N-phenyl maleimide; which similarly applies hereinafter), and an antioxidant (b-1) content of 500 ppm was prepared by dissolving 9 g of the N-phenyl maleimide in 6 g of acrylonitrile having a water content of 0.005% by weight,
15 then adding 4.5 mg of pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] [antioxidant (a-1)] and 4.5 mg of tristearyl phosphite [antioxidant (b-1)] to the resultant solution, and adjusting the water content of the produced mixture.

[0058]

20 When the acrylonitrile solution in one of the test tubes was tested for the L, a, and b values after the preparation, L = 99.3, a = -21.0, and b = 39.0 were obtained. The other test tube, with the gaseous phase part of the acrylonitrile solution displaced with nitrogen gas containing 7% by volume of molecular oxygen, was used
25 for the forced coloration test contemplated by this invention. After 3 days' (72 hours') standing, the test piece was extracted from the test tube and the acrylonitrile solution left in the test tube was measured for the L, a, and b values. The results were L = 98.6, a = -19.8, and b = 41.2 and the differences in the L, a,
30 and b values before and after the test were $\Delta L = 0.7$, $\Delta a = 1.2$, and $\Delta b = 2.2$. The solution after the test was transparent. The results are shown in Table 1.

[0059]

Example 2

An acrylonitrile solution shown in Table 1 was prepared by following the procedure of Example 1 while using triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate] [antioxidant (a-2)] and trisnonylphenyl phosphite [antioxidant (b-2)] instead as antioxidants. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 1.

[0060]

Example 3

An acrylonitrile solution shown in Table 1 was prepared by following the procedure of Example 1 while using octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate [antioxidant (a-3)] and distearyl pentaerythritol diphosphite [antioxidant (b-3)] instead as antioxidants. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 1.

Example 4

An acrylonitrile solution shown in Table 1 was prepared by following the procedure of Example 1 while using 4-tert-butyl catechol [antioxidant (a-4)] and distearyl pentaerythritol diphosphite [antioxidant (b-3)] instead as antioxidants and further using N,N'-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl] hydrazine [inactivating agent (c-1)] as a metal-inactivating agent. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 1.

[0061]

Example 5

An acrylonitrile solution shown in Table 1 was prepared by following the procedure of Example 1 while using triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate] [antioxidant (a-2)] and distearyl pentaerythritol diphosphite [antioxidant (b-3)] instead as antioxidants and further using 2,2'-oxamide-bis[ethyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (inactivating agent (c-2)] as a metal-inactivating agent. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 1.

[0062]
[Table 1]

Table 1

Example	1	2	3	4	5
Antioxidant					
Kind	a - 1	a - 2	a - 3	a - 4	a - 2
Amount added	500	500	1000	100	1000
Kind	b - 1	b - 2	b - 3	b - 3	b - 3
Amount added	500	500	1000	1000	1000
Metal-inactivating agent					
Kind	-	-	-	c - 1	c - 2
Amount added				500	1000
Water content in solution	0.1	0.2	0.2	0.1	0.2
Molecular oxygen concentration	7	7	7	21	5
Clarity of solution after test	trans-parent	trans-parent	trans-parent	trans-parent	trans-parent
L, a, and b values					
L	99.3	99.3	99.3	99.3	99.3
a	-21.3	-21.3	-21.3	-21.3	-21.3
b	39.0	39.0	39.0	39.0	39.0
Difference before and after test					
ΔL	0.7	0.8	0.5	0.5	0.4
Δa	1.2	2.8	0.8	1.2	0.5
Δb	2.2	3.5	1.8	2.8	1.0

Amount of the antioxidant and metal-inactivating agent added:

5 ppm (based on N-phenyl maleimide)

Water content in solution: % by weight

Molecular oxygen concentration: % by volume (in gaseous phase part)

(a-1):Pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate

(a-2):Triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-

10 hydroxyphenyl)propionate]

(a-3):Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate

(a-4):4-Tert-butyl catechol

(b-1):Tristearyl phosphite

(b-2):Trisnonylphenyl phosphite

15 (b-3):Distearyl pentaerythritol diphosphite

(c-1):N,N'-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]hydrazine

(c-2):2,2'-Oxamide bis[ethyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]

[0063]

Example 6

An acrylonitrile solution shown in Table 2 was prepared by following the procedure of Example 1 while using 4-tert-butyl catechol [antioxidant (a-4)] and di(2-ethylhexyl) phosphate [antioxidant (b-4)] instead as antioxidants. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 2.

[0064]

Example 7

An acrylonitrile solution shown in Table 2 was prepared by following the procedure of Example 1 while using triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate] [antioxidant (a-2)] and distearyl pentaerythritol diphosphite [antioxidant (b-3)] instead as antioxidants and 2,2'-oxamide bis[ethyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] [inactivating agent (c-2)] as a metal-inactivating agent. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 2.

[0065]

Example 8

An acrylonitrile solution shown in Table 2 was prepared by following the procedure of Example 1 while using triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate] [antioxidant (a-2)] and distearyl pentaerythritol diphosphite [antioxidant (b-3)] instead as antioxidants and 2,2'-oxamide bis[ethyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] [inactivating agent (c-2)] as a metal-inactivating agent. The

acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 2.

5 [0066]

Example 9

An acrylonitrile solution shown in Table 2 was prepared by following the procedure of Example 1. The acrylonitrile solution was tested to determine the L, a, and b values and the differences
10 of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 2.

[0067]

Example 10

An acrylonitrile solution shown in Table 2 was prepared by
15 following the procedure of Example 1 while using 1,6-hexanediol-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] [antioxidant (a-5)] instead as antioxidants. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in
20 the same manner as in Example 1. The results are shown in Table 2.

[0068]

[Table 2]

Table 2

Example	6	7	8	9	10
Antioxidant					
Kind	a - 4	a - 2	a - 2	-	a - 5
Amount added	100	1000	1000		1000
Kind	b - 4	b - 3	b - 3	-	-
Amount added	1000	1000	1000		
Metal-inactivating agent					
Kind	-	c - 2	c - 2	-	-
Amount added		1000	500		
Water content in solution	0.18	0.05	0.002	0.02	0.2
Molecular oxygen concentration	5	5	5	21	5
Clarity of solution after test	trans-parent	trans-parent	trans-parent	trans-parent	trans-parent
L, a, and b values					
L	99.3	99.3	99.3	99.3	99.3
a	-21.0	-21.0	-21.0	-21.0	-21.0
b	39.0	39.0	39.0	39.0	39.0
Difference before and after test					
ΔL	0.5	0.3	0.1	0.7	1.2
Δa	1.2	0.3	0.1	1.5	1.0
Δb	1.5	0.5	0.3	3.5	2.4

5 (a-5):1,6-Hexanediol-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]

(b-4):Di(2-ethylhexyl) phosphate

The other agents are the same as those shown in Table 1.

[0069]

Example 11

An acrylonitrile solution shown in Table 3 was prepared by following the procedure of Example 1 while using triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate] [antioxidant (a-2)] and distearyl pentaerythritol diphosphite [antioxidant (b-3)] instead as antioxidants. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 3.

[0070]

Example 12

An acrylonitrile solution shown in Table 3 was prepared by following the procedure of Example 1 while using distearyl pentaerythritol diphosphite [antioxidant (b-3)] instead as antioxidants. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 3.

[0071]

Example 13

An acrylonitrile solution shown in Table 3 was prepared by following the procedure of Example 1. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 3.

[0072]

Example 14

An acrylonitrile solution shown in Table 3 was prepared by following the procedure of Example 1 while using 2,2'-oxamide bis[ethyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]

[inactivating agent (c-2)] as a metal-inactivating agent. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in
5 Table 3.

[0073]

Example 15

An acrylonitrile solution shown in Table 3 was prepared by following the procedure of Example 1 while using 2,2'-oxamide
10 bis[ethyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]
[inactivating agent (c-2)] as a metal-inactivating agent. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in
15 Table 3.

[0074]

[Table 3]

Table 3

Example	11	12	13	14	15
Antioxidant					
Kind	a - 2	-	-	-	-
Amount added	1000				
Kind	b - 3	b - 3	-	-	-
Amount added	500	1000			
Metal-inactivating agent					
Kind	-	-	-	c - 2	c - 2
Amount added				500	500
Water content in solution	0.2	0.2	0.005	0.05	0.01
Molecular oxygen concentration	21	21	5	21	7
Clarity of solution after test	trans-parent	trans-parent	trans-parent	trans-parent	trans-parent
L, a, and b values					
L	99.3	99.3	99.3	99.3	99.3
a	-21.0	-21.0	-21.0	-21.0	-21.0
b	39.0	39.0	39.0	39.0	39.0
Difference before and after test					
ΔL	0.8	1.0	0.8	0.7	0.3
Δa	1.3	1.6	0.5	0.9	0.5
Δb	2.5	3.6	1.8	1.7	1.2

The symbols and the like are the same as those of Table 1.

[0075]

Example 16

An acrylonitrile solution shown in Table 4 was prepared by following the procedure of Example 1 while using di(2-ethylhexyl) phosphate [antioxidant (b-4)] instead as antioxidants and N,N'-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl] hydrazine [inactivating agent (c-1)] as a metal-inactivating agent. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 4.

[0076]

Example 17

An acrylonitrile solution shown in Table 4 was prepared by following the procedure of Example 1 while using distearyl pentaerythritol diphosphite [antioxidant (b-3)] instead as antioxidants and 2,2'-oxamide bis[ethyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] [inactivating agent (c-2)] as a metal-inactivating agent. The acrylonitrile solution was tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 4.

[0077]

[Table 4]

Table 4

Example	16	17
Antioxidant		
Kind	-	-
Amount added		
Kind	b - 4	b - 3
Amount added	1000	1000
Metal-inactivating agent		
Kind	c - 1	c - 2
Amount added	1000	500
Water content in solution	0.1	0.25
Molecular oxygen concentration	21	5
Clarity of solution after test	transparent	transparent
L, a, b values		
L	99.3	99.3
a	-21.0	-21.0
b	39.0	39.0
Difference before and after test		
ΔL	0.8	0.7
Δa	1.0	1.5
Δb	2.4	2.9

The symbols and the like are the same as those shown in
5 Table 1 and Table 2.

[0078]

Controls 1 to 3

Acrylonitrile solutions shown in Table 5 were prepared. The acrylonitrile solutions were tested to determine the L, a, and b values and the differences of the L, a, and b values before and after the test in the same manner as in Example 1. The results are shown in Table 5.

[0079]

[Table 5]

10

Table 5

Control	1	2	3
Antioxidant			
Kind	-	-	-
Amount added			
Kind	-	-	-
Amount added			
Metal-inactivating agent			
Kind	-	-	-
Amount added			
Water content in solution	0.15	0.2	0.8
Molecular oxygen concentration	21	5	5
Clarity of solution after test	transparent	transparent	white cloudy
L, a, b values			
L	99.3	99.3	99.3
a	-21.0	-21.0	-21.0
b	39.0	39.0	39.0
Difference before and after test			
ΔL	6.2	3.6	10.7
Δa	6.5	5.2	6.7
Δb	10.4	8.5	10.5

The symbols and the like are the same as those shown in Table 1.

[0080]

Example 18

In a four-neck flask having an inner volume of one liter and provided with a stirrer, a condenser, a nitrogen gas inlet tube, and a dropping funnel, 38.4 g of styrene and 269.3 g of toluene (both guaranteed reagents; produced by Wako Pure Chemical Industries, Ltd.) were placed and, after the subsequent thorough displacement of the gaseous phase part with nitrogen, heated to 90°C. To the resultant solution in the flask, a mixed solution comprising 172.7 g of the acrylonitrile solution of N-phenyl maleimide obtained in Example 4 and 54.3 g of toluene, 102.4 g of styrene, and a solution consisting of 0.26 g of benzoyl peroxide (produced by Nippon Oils & Fats Co., Ltd.) and 12.2 g of toluene were drip-fed through the dropping funnel over a period of 3 hours, with the inner temperature of the tube kept at 90°C. After the completion of this drip-feeding, the contents of the tube were continuously stirred for 1.5 hours.

[0081]

Then, a part of the reaction product was extracted, diluted with methylethyl ketone, and then reprecipitated in methanol by a standard technique. The polymer consequently precipitated was filtered and dried, subjected to the measurement with a melt indexer (produced by Techno Seven K.K. and marketed under product code of "Type L240"), heated at 240°C for 4 hours, and then molded into strands. By visual observation, the strands of polymer were found to have a light yellow clear appearance.

[0082]

Control 4

Strands of a polymer were obtained by following the procedure of Example 18 while using the acrylonitrile solution of N-phenyl maleimide obtained in Control 1 instead. The polymer had a yellow brown appearance and showed a clear sign of coloration.

[0083]

[Effects of the Invention]

The acrylonitrile solution of maleimides of this invention is transparent, is not colored nor opacified during the course of handling, and has excellent stability.

5 [0084]

According to the method of this invention, the above-mentioned acrylonitrile solution of maleimides can be effectively prepared.

[0085]

By using the acrylonitrile solution of maleimides with
10 excellent transparency as mentioned above, a acrylonitrile-
maleimides-containing copolymer with excellent color tone can be
obtained.

[0086]

[DOCUMENT'S NAME] ABSTRACT

[ABSTRACT]

[Problems] To provide an acrylonitrile solution of maleimides which is transparent, is not colored nor opacified during the course of handling, and has excellent stability, a method for the preparation thereof, and an acrylonitrile-maleimide containing copolymer obtained by the use of the acrylonitrile solution.

[Solving Means] (a) An acrylonitrile solution of maleimides whose values, ΔL , Δa , and Δb , before and after a forced coloration test, (absolute value) are respectively not more than 5, not more than 5, and not more than 10. (b) This acrylonitrile solution of maleimides can be prepared by adjusting the water content of the acrylonitrile solution to a level of not more than 0.1% by weight, or allowing the presence in the acrylonitrile solution of at least one member selected among hindered phenols and at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides, or adjusting the water content of the acrylonitrile solution to a level of not more than 0.3% by weight and allowing the presence in the acrylonitrile solution of at least one member selected among hindered phenols or at least one member selected from the group consisting of phosphorous esters, phosphoric esters, and phosphoric acid amides.

[Drawing to be Selected] None

[Document's Name] EX OFFICIO CORRECTION DATA

[Document to be corrected] Application for Patent

5 <Information to be acknowledged or added>

[Applicant for Patent] Applicant

[Identification Number] 000004628

[Domicile or Residence] 1-1, Koraihashi 4-chome, Chuo-ku,
Osaka-shi, Osaka-fu

10 [Name] Nippon Shokubai Co., Ltd.